



Rec'd PCT/PTO 03 MAY 2005

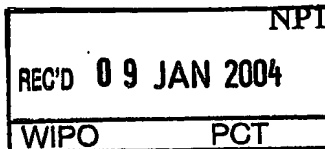
G803/4894



INVESTOR IN PEOPLE

PRIORITY DOCUMENT
SUBMITTED OR TRANSMITTED IN
COMPLIANCE WITH
RULE 17.1(a) OR (b)

The Patent Office
Concept House
Cardiff Road
Newport
South Wales
NP10 8QQ

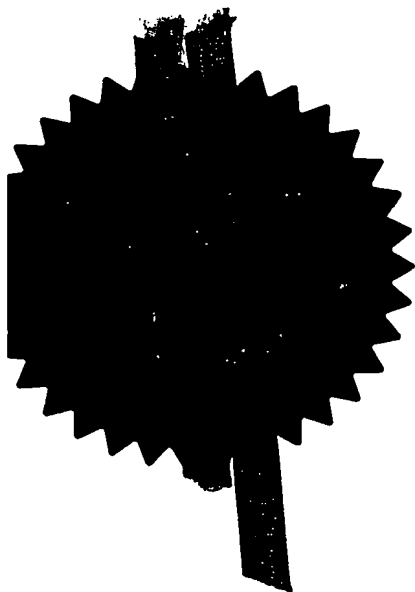


I, the undersigned, being an officer duly authorised in accordance with Section 74(1) and (4) of the Deregulation & Contracting Out Act 1994, to sign and issue certificates on behalf of the Comptroller-General, hereby certify that annexed hereto is a true copy of the documents as originally filed in connection with the patent application identified therein.

In accordance with the Patents (Companies Re-registration) Rules 1982, if a company named in this certificate and any accompanying documents has re-registered under the Companies Act 1980 with the same name as that with which it was registered immediately before re-registration save for the substitution as, or inclusion as, the last part of the name of the words "public limited company" or their equivalents in Welsh, references to the name of the company in this certificate and any accompanying documents shall be treated as references to the name with which it is so re-registered.

In accordance with the rules, the words "public limited company" may be replaced by p.l.c., plc, P.L.C. or PLC.

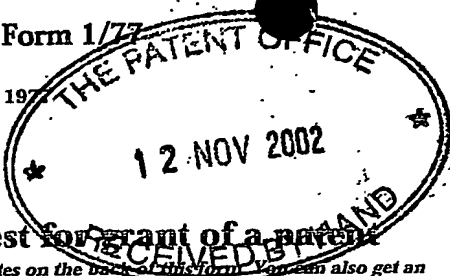
Re-registration under the Companies Act does not constitute a new legal entity but merely subjects the company to certain additional company law rules.



Signed

Andrew Gurney

Dated 28 November 2003



The
Patent
Office

13NOV02 E762906-30 D02890
_P01/7700 0.00-0226383.8

The Patent Office

Cardiff Road
Newport
South Wales
NP9 1RH

Request for grant of a patent

(See the notes on the back of this form. You can also get an explanatory leaflet from the Patent Office to help you fill in this form)

112 NOV 2002

1. Your reference

REP07316GB

2. Patent application number

(The Patent Office will fill in this part)

0226383.8

3. Full name, address and postcode of the or of each applicant (underline all surnames)

Sherwood Technology Ltd.
Heathcoat Building
Nottingham Science & Technology Park
University Boulevard
Nottingham
NG7 2QJ

Patents ADP number (if you know it)

8092579001

If the applicant is a corporate body, give the country/state of its incorporation

United Kingdom

4. Title of the invention

TRANSITION METAL COMPOUNDS AND THEIR USE
IN IMAGEABLE COATINGS

5. Name of your agent (if you have one)

Gill Jennings & Every

"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)

Broadgate House
7 Eldon Street
London
EC2M 7LH

Patents ADP number (if you know it)

745002

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and (if you know it) the or each application number

Country

Priority application number
(if you know it)

Date of filing
(day / month / year)

7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application

Date of filing
(day / month / year)

8. Is a statement of inventorship and of right to grant of a patent required in support of this request? (Answer 'Yes' if:

YES

- a) any applicant named in part 3 is not an inventor, or
 - b) there is an inventor who is not named as an applicant, or
 - c) any named applicant is a corporate body.
- See note (d))

Patents Form 1/77

9. Enter the number of sheets for any of the following items you are filing with this form. Do not count copies of the same document

Continuation sheets of this form

Description

9

Claim(s)

1

Abstract

Drawing(s)

10. If you are also filing any of the following, state how many against each item.

Priority documents

Translations of priority documents

Statement of inventorship and right to grant of a patent (*Patents Form 7/77*)

Request for preliminary examination and search (*Patents Form 9/77*)

Request for substantive examination (*Patents Form 10/77*)

Any other documents
(please specify)

NO

11. For the applicant
Gill Jennings & Every

I/We request the grant of a patent on the basis of this application.

Signature

Date

12 November 2002

12. Name and daytime telephone number of person to contact in the United Kingdom

R E Perry

020 7377 1377

Warning

After an application for a patent has been filed, the Comptroller of the Patent Office will consider whether publication or communication of the invention should be prohibited or restricted under Section 22 of the Patents Act 1977. You will be informed if it is necessary to prohibit or restrict your invention in this way. Furthermore, if you live in the United Kingdom, Section 23 of the Patents Act 1977 stops you from applying for a patent abroad without first getting written permission from the Patent Office unless an application has been filed at least 6 weeks beforehand in the United Kingdom for a patent for the same invention and either no direction prohibiting publication or communication has been given, or any such direction has been revoked.

Notes

- a) If you need help to fill in this form or you have any questions, please contact the Patent Office on 0645 500505.
- b) Write your answers in capital letters using black ink or you may type them.
- c) If there is not enough space for all the relevant details on any part of this form, please continue on a separate sheet of paper and write "see continuation sheet" in the relevant part(s). Any continuation sheet should be attached to this form.
- d) If you have answered 'Yes' Patents Form 7/77 will need to be filed.
- e) Once you have filled in the form you must remember to sign and date it.
- f) For details of the fee and ways to pay please contact the Patent Office.

TRANSITION METAL COMPOUNDS AND THEIR USE
IN IMAGEABLE COATINGS

Field of the Invention

This invention relates to transition metal compounds and their use in
5 imageable coatings.

Background of the Invention

For many years, heat sensitive imaging sheets have been used for
copying, thermal printing, thermal recording and thermal labelling. More recently,
the development of scribing lasers has enabled the use of thermally-sensitive
10 imaging materials for the coding and marking of both sheet materials and shaped
objects that may or may not be self-supporting.

Two classes of colour-forming reactants have commonly been used for
thermographic materials, i.e. leuco lactone or spiropyran compounds normally
developed by phenolic compounds, e.g. as described in US-A-3846153, and
15 heavy metal salts of organic acids reactable with ligands to give coloured
complexes, e.g. as described in US-A-2663654. The use of both these types of
compounds depends on effecting a physical separation of the solid components,
through dispersing them in a polymer binder, coating them on a suitable support,
and melting at least one of them to cause colour formation. When coated and
20 dried dispersions of solid materials, by their nature, result in layers of some
opacity. This is normally acceptable on opaque substrates such as paper, but
limits applications on transparent substrates such as clear Mylar (polyester) film
and transparent packaging films. Examples of such applications are where a film
transmission original is required or, in transparent film packaging applications,
25 where film opacity would obscure sight of the packaging contents or container
surface.

There is therefore a need for transparent, thermally-sensitive imaging
layers for coating to transparent or semi-transparent film supports and reflective
supports such as can-metal. Further, there is a need for transparent laser-
30 sensitive imaging materials that may be coated or printed on shaped or formed
objects such as bottles and other containers for labelling or coding applications.
Naturally for the applications mentioned above, the coatings should adhere to

the substrate firmly and be robust, i.e. have good resistance to the types of chemical and physical treatment encountered in the end use environment. In general, organic solvent-based compositions containing solvent-soluble binders give, on drying, tougher, better adhering layers of greater transparency and water-resistance than like water-based compositions.

The use of organic amine molybdates in thermal imaging layers is described in US-A-2910377 (see Example 10) and US-A-3028255 (where the exemplified amines are primary amines). This use is confined to copy paper sheets, and the molybdate is dispersed by prolonged ball-milling in a resinous binder to give a suspension, used for coating. Such a suspension when coated and dried on a transparent film support, would cause loss of transparency.

US-A-4217409 (see Examples 10 and 12) describes the use of isopropylammonium molybdate in an acidic aqueous solution of polyvinyl alcohol as a coating that, when applied to a substrate, gives a laminar material sensitive to electromagnetic radiation including IR, visible and UV radiation. Polyvinyl alcohol solutions often have poor coating properties towards polyester film and the hazy dried films detach readily. The dried and imaged coating would also be susceptible to physical and chemical damage, most notably chemical damage from water. Isopropylamine is volatile and would cause odour should the material be contacted with aqueous alkali.

US-A-4406839 describes the synthesis of organic solvent-soluble amine molybdates useful as smoke retardants and made from a variety of amines. Examples employ high molecular weight amines such as tridodecylamine.

Amine molybdates, their synthesis and uses, are also described in US-A-2910377, US-A-3028255, US-A-3290245, US-A-4053455, US-A-4153792, US-A-4217292, US-A-4217409, US-A-4226987, US-A-4266051, US-A-4406837, US-A-4406838, US-A-4406839, US-A-4406840, US-A-4410462, US-A-4410463, US-A-4424164, US-A-4425279, US-A-6217797 and US-A-6355277.

Summary of the Invention

The present invention is based at least in part on the finding that amine molybdates and analogous compounds, some of which may be new, have properties that render them suitable for imaging. In particular, they are soluble

in at least some organic solvents, are compatible with film-forming solvent-soluble organic binders, and give solutions that, when coated on an inert substrate such as clear Mylar polyester film and dried, form a continuous substantially visible light-transparent layer on the support. Such layers are thermally sensitive and find utility in thermographic materials for imaging by scanning laser or thermal printer, to provide effective marking, without opacification in the non-image areas.

According to one aspect of this invention, a process for forming an image on a substrate, comprises coating the substrate with a solution, in an organic solvent, of an amine compound of molybdenum, tungsten or vanadium, wherein the compound changes colour on heating irradiation, and heating or irradiating the coating.

A further aspect of the invention is a coated substrate, wherein the amine is a secondary or tertiary alkylamine in which each alkyl group has up to 12 carbon atoms and the amine has up to 24 carbon atoms. Other aspects are solutions of the amine compound and a photopolymerisable monomer or a thermoplast.

Description of Preferred Embodiments

Preferred compounds for use in the invention are amine molybdates. The term "amine molybdate" (of which an example is ethylamine molybdate) is used herein to describe compounds whose structure may be ill-defined, and which are also sometimes called the corresponding ammonium molybdates (e.g. ethylammonium molybdate), which implies that the compounds are salts. The generic term "amine molybdate" refers to complexes or salts formed on reacting an amine to give an amine molybdate or amine isopolymolybdate. For reference, see Cotton & Wilkinson; Advanced Inorganic Chemistry 2nd Edition 1967 Chapter 30 Section 30-C-2&3.

It will be understood that one or more amine compounds may be used in the invention. Amine molybdates will be described herein, for the purpose of illustration. Such compounds for use in the invention are formed from amines and molybdate and polymolybdate(VI)acids and their salts and can be thermally activated in a coating, to give an image.

More specifically, such compounds are made, for example, using known saturated secondary or tertiary aliphatic dialkyl or trialkyl monoamines having boiling points at 1 atmosphere pressure equal to or above 150°C and melting points below about 80°C and with alkyl groups having from 3 to 12 carbon atoms, preferably 5 to 10 carbon atoms. Typically, the compound has a total of 7 to 24 C atoms. Salts of the compounds may also be used, such as amine acetates or chlorides. Representative amines are dipentylamine, tripentylamine, di-n-hexylamine, tri-n-hexylamine, bis(2-ethylhexyl)amine, di-n-octylamine and tri-n-octylamine.

The amine molybdates are made by reacting the amine with a molybdenum compound, e.g. in oxidation state VI, such as molybdenum trioxide, molybdic acid, ammonium dimolybdate, ammonium heptamolybdate, ammonium octamolybdate, sodium molybdate or commercial "molybdic acid" (which primarily consists of one or more ammonium molybdates). A representative amine molybdate of the invention is bis(2-ethylhexyl)amine octamolybdate.

Amine molybdates of the invention have one or more of the following properties:

- Individually soluble in at least one organic solvent
- Transparent or near transparent film-forming properties on specified commercial polymer substrates when applied by coating or printing an organic solvent solution
- Thermal sensitivity manifested as a colour change of good visual discrimination when a layer comprising the amine molybdate is exposed thermally imagewise by a scanning laser and/or heat block imaged by a thermal printer
- Compatibility with at least one solvent soluble binder polymer as indicated by the formation of a near transparent film of a blend
- Preparation using an amine precursor of low volatility, so that there is low risk of a hazard if the amine molybdate layer is exposed to aqueous alkali and the amine is released

The amine molybdates are soluble in organic solvents, are compatible with film-forming solvent soluble organic binders and give solutions that when

coated or printed on an inert substrate such as clear Mylar polyester film and dried, form a continuous layer of the amine molybdate that is substantially transparent to visible light. Such layers are thermally sensitive and find utility in thermographic materials and on 3D objects for imaging by scanning laser or thermal printer. Clear layers formed by means of the invention may also be useful on opaque substrates because they can impart desirable gloss, as distinct from compositions containing suspended insoluble molybdates that give matt surfaces.

Imaging elements comprising these amine molybdates may be supported on a flexible sheet substrate, preferably a flexible transparent sheet substrate such as polyester. Alternatively a rigid 3D object substrate may be used such as the external surface of a container. There should be a good adhesive bond between imaging element and substrate. The substrate should be able to withstand laser imaging of the element (comprising the amine molybdates) without unacceptable degradation or deformation upon laser or thermal imaging. Preferred substrates are transparent or translucent materials that absorb the IR radiation output of the laser to some extent: otherwise the substrate may act as a heat sink to the laser-exposed areas of the imaging element, reducing layer sensitivity. In this respect Mylar polyester film is better than unfilled polypropylene or polyethylene.

The solvent-soluble molybdates used in the invention can be applied from solution and dried to give a near transparent layer. Film-forming compositions containing these amine molybdates give layers having good adhesion transparency and imagewise thermal sensitivity. Such layers can have filmogenic and transparency properties, e.g. on commercial transparent polymer film supports such as clear Mylar and polypropylene, providing giving near-transparent thermally sensitive sheet or web materials.. The solvent-soluble amine molybdates also show good compatibility when blended with specified organic solvent-soluble polymeric binders; these blends can also form useful substantially transparent thermally sensitive layers, to provide thermographic materials.

The organic solvent solubility properties of the amine molybdates of the invention permit the avoidance of the time-consuming, wasteful and costly milling processes normally involved in the preparation of coating mixtures for prior art thermally sensitive imaging materials and enables thermally sensitive layers of good transparency and gloss to be made on transparent substrates such as Mylar and commercially available packaging films such as polypropylene.

The invention also provides amine molybdate compositions that, when applied as a solvent coating to commercially available transparent film or supports or otherwise incorporated on or within transparent or semi transparent polymer layers, give direct thermally sensitive imaging media having excellent stability transparency and sensitivity properties for thermal laser imaging or appropriate thermal printing. The coating weight of the dry coating is normally in the range 0.5 to 20 g/m², preferably 1 to 10 g/m².

The invention also provides thermally sensitive imaging materials comprising a layer comprising the amine molybdate, adhering to a substrate or within a substrate which is preferably an optically near-transparent or translucent polymeric material. Suitable substrates include paper, laminates and films of the type described above. Another aspect of this invention is thermally imageable materials comprising the amine molybdate and incorporated on a substrate.

Amine molybdates may also be useful in dispersed form in a thermographic layer. Some are readily dispersed in water, and could be used, say, on an opaque substrate like paper to give a matt layer. Thus, depending on the conditions, the amine molybdates could be used for both transparent/glossy materials and also opaque/matt materials).

Thermally imageable materials comprising an amine molybdate in solid solution or dispersion in a molten material comprising a thermoplastic polymer, can be made by cooling the material whilst rolling it flat or forming it into a shape, such as the shape of a container.

Thermally imageable materials comprising an amine molybdate in solution or dispersion in a liquid photopolymerisable composition may be made by photopolymerising the composition.

It will be appreciated by one of ordinary skill in the art that it is possible to incorporate additives of various sorts in the imaging layers, and which might be beneficial in certain circumstances. Such additives include, for example, polymer binders, mild reducing agents to promote thermal printer performance, colorants such as dyes or pigments, antioxidants and other known stabilisers, antiblocking materials such as talc or selected silicas, and materials adsorbent to or reactive with any thermolysis products of laser imaging.

An additive of particular utility, in solution or suspension or in a separate layer, is an electron-donating dye precursor often known as a colour-former. When amine molybdates are incorporated in a layer with such colour-formers and thermally imaged using a CO₂ laser, coloured images may be obtained. The colour corresponds to that obtained by the use of common colour developers such as certain phenols. Weak block images may also be obtained, e.g. using a heat sealer at 100-120 C and contact times of 1-10 seconds. Thus the amine molybdate acts as an electron acceptor and colour developer for at least some of these colour-formers.

Protective polymer or other layers on the imaging layer may be useful in some circumstances. Such layers may prevent or reduce for example mechanical or chemical damage to the unexposed or exposed thermally sensitive layers of the invention. Layers comprising mild reducing agents may also be added to promote thermal printer performance. Such layers may also act to reduce emanation of any thermolysis products of laser imaging. Such layers can be applied by known means such as lamination or coating.

The following Examples illustrate the invention.

Example 1 Bis(2-ethylhexyl)amine octamolybdate

The following synthesis is adapted from the method given in US-A-4217292 (Example 3) for dodecylammonium octamolybdate.

In a 500 ml flange flask vessel was weighed molybdenum trioxide (15.53 g; Aldrich 99%; 10-20 µm particle size by Fisher sub-sieve sizer), deionised water (300 g) and ammonium chloride (8.6 g) (Aldrich reagent). The mixture was stirred vigorously while bis(2-ethylhexyl) amine (13.03 g; Aldrich) was added dropwise over 10 minutes. The vessel contents were then heated to reflux with

stirring and refluxed for 4 hrs. A pale green-blue tarry material formed that part adhered to the vessel walls. On cooling, the reaction mixture to room temperature, the tarry product formed a glass-like solid. The solid was collected by filtration with some manipulative loss, ground and washed successively with
5 deionised water and finally with isopropanol. Finally the pale green-blue product was dried in an oven for 24 hrs at 65°C. Yield was 26.2 g. It was readily soluble in 2-butanone to give a pale-green solution. A trace of white material (perhaps unreacted MoO_3) remained undissolved.

Example 2 Coating Composition Without Polymer Binder

10 Bis(2-ethylhexyl)amine octamolybdate (10 g) was dissolved in 2-butanone (30 g). The solution was separated from a trace of insoluble white solid impurity to give a solution that can be used as a coating composition of the invention.

Example 3 Thermally Imageable Material

The solution prepared in Example 2 was coated on each of four supports,
15 i.e. opaque white (titanium dioxide-filled) Mylar film, clear Mylar (polyethylene terephthalate) film, domestic aluminium foil, and polypropylene packaging film (UCB). This was done using a wire coating bar, giving a 12 μm on wet film, and dried using warm air to give a thermally imageable material.

Continuous glossy well-bonded films were obtained in each case. The
20 coatings on clear Mylar and polypropylene were transparent and all were non-tacky when cool. The dry coating weights were found to be about 3 g /m². The resulting coated materials were exposed imagewise using a CO₂ scribing laser beam of 0.3 mm diameter at a scan speed of 1000 mm/sec. A distinct grey-black image of alphanumeric characters was obtained when the power was set at 3-4
25 Watts for Mylar and aluminium foil substrates. The images were less legible at 2 Watts, indicating sub-optimum exposure. With the polypropylene substrate, images were obtained at about 6W.

Example 4 Coating Composition Containing Polymer Binder

A solution of bis(2-ethylhexyl)amine octamolybdate (10 g) was dissolved
30 in 2-butanone (30 g). The solution was separated from a trace of insoluble white solid impurity. 4 g of this solution was mixed with 4 g of a 15% by weight

solution of Elvacite 2041 (a methyl methacrylate homopolymer resin grade manufactured by INEOS) binder in 2-butanone to give a coating solution.

Example 5 Thermally Imageable Film

The solution of Example 4 was coated on packaging grade polypropylene film using a wire-wound bar (giving a nominal 12 μm wet film thickness) and dried using warm air to give a transparent coated film. The transparency observed indicates good compatibility of the amine molybdate and the acrylic binder. The dry coating weight was found to be 2.8 g/m^2 . The resulting coated film of the invention had high transparency. It was exposed imagewise using a CO_2 scribing laser beam of 0.3 mm diameter at a scan speed of 1000 mm/sec. A distinct grey-black image of alphanumeric characters was obtained when the power was set at 3-4 Watts. Some lifting of the image was observed at 4 Watts. The image was less legible at 2 Watts, indicating inadequate exposure.

Example 6 Red Thermographic Film

To 0.4g of a 25% by weight solution of bis(2-ethylhexylamine) octamolybdate in 2-butanone was added with thorough mixing 1.0g of a 33.3% by weight solution of Elvacite 2044 also in 2-butanone (Elvacite 2044 is a n-butylmethacrylate-based acrylic resin manufactured by INEOS Acrylics). In this composition was dissolved by agitation 0.1g of a commercial electron-donating colour-former (Pergascript Red I-6B manufactured by Ciba Specialty Chemicals and described as a bisindolyl phthalide compound). The resulting pale yellowish-pink solution was coated on clear Mylar film using a 25 wire bar and dried using warm air. A transparent film resulted.

A pale red image resulted on block imaging the film at 100°C using a heat sealer and a contact time of 10 seconds. A distinct red image resulted from imaging the film using a CO_2 scribing laser beam of 0.3mm diameter at a scan speed of 1000 mm / second and set at 3 Watts power.

CLAIMS

1. A process for forming an image on a substrate, which comprises coating the substrate with a solution, in an organic solvent, of an amine compound of molybdenum, tungsten or vanadium that changes colour on heating or irradiation, and heating or irradiating the coating.
2. A process for forming an image on a substrate, which comprises coating the substrate with an aqueous dispersion or suspension, of an amine compound of molybdenum, tungsten or vanadium that changes colour on heating or irradiation, and heating or irradiating the coating.
3. A process according to claim 1 or claim 2, wherein the amine compound is of molybdenum (VI).
4. A process according to claim 3, wherein the amine is a secondary or tertiary alkylamine in which each alkyl group has up to 12 carbon atoms and the amine has up to 24 carbon atoms.
5. A process according to any preceding claim, wherein the coating also comprises the use of an organic polymer binder.
6. A process according to any preceding claim, wherein the coating also comprises the use of a colour-former, e.g. a substantially colourless electron-donating dye precursor.
7. A coated substrate, wherein the coating is a substantially visible light-transparent layer comprising an amine compound as defined in any of claims 1 to 4, and optionally also an additional component as defined in claim 5 or claim 6, and optionally including an image formed therein by heating or irradiation.
8. A coated substrate according to claim 7, wherein the substrate is also substantially transparent to visible light.
9. A solution of an amine compound as defined in any of claims 1 to 4 and of a thermoplastic polymer.
10. A solution of an amine compound as defined in any of claims 1 to 4 and of a photopolymerisable monomer.
11. A solution according to claim 10, which is fluid at or below 150°C.